

1 **TITLE**

2 High Contrast Surface Marking Using Irradiation of
3 Electrostatically Applied Marking Materials

7 **CROSS REFERENCES TO RELATED PATENTS**

9 This application is a continuation-in-part of U.S. App.
10 Ser. No. 09/477,921, filed January 5, 2000 and now issued as
11 U.S. Pat. No. _____, which is a divisional application of
12 U.S. App. Ser. No. 08/925,031, filed September 8, 1997 and
13 issued as U.S. Pat. No. 6,075,223 on June 13, 2000.
14 International application PCT/US98/18720, filed on September
15 8, 1998 and published as WO 99/16625 on April 8, 1999,
16 claimed priority from USSN 08/925,031.

18 **FIELD OF INVENTION**

19 The present invention relates to a method of producing
20 permanent, enhanced contrast and/or color markings formed as
21 a new marking layer on top of substrates including glass,
22 ceramic, porcelain, metal, and plastic. A laser beam or
23 other suitable radiant energy source irradiates a marking
24 medium having a glass frit containing an energy absorbing
25 enhancer, or alternatively the marking medium can be a mixed
26 metal oxide or a mixed organic pigment. This invention
27 further relates to a method of producing permanent enhanced
28 contrast and/or color markings formed as a new marking layer
29 on top of both electrically conductive and non-conductive
30 substrate materials by electrostatically coating said
31 substrate materials and irradiating said coating with a
32 laser beam in accordance with the form of a mark or
33 decoration to be produced. In particular, this invention

1 pertains to the application of laser marking materials in a
2 controlled pattern of finely separated, charged coating
3 particles projected toward an electrically-isolated and/or
4 oppositely-charged substrate material.

5

6 **BACKGROUND OF THE INVENTION**

7 The marking of ceramic materials, glazes and glasses
8 can be effected by conventional marking and decoration
9 methods such as etching, cutting, engraving, grinding or by
10 applying a glass or glaze colorant. In these methods, the
11 surface of the marked material is altered with the
12 consequence that the material may suffer damage, especially
13 if marking is effected by etching, engraving, or cutting.
14 The application of a glass or glaze colorant necessitates,
15 in addition, a second firing step. The markings so produced
16 are not always satisfactory in all respects.

17 It is also known to mark glass by means of a laser
18 beam, whereas the known methods are based on melting or
19 removing substrate material such that the surface of the
20 marked material is also altered.

21 German Offenlegungsschrift 3 539 047 postulates a
22 method of decorating, marking, and engraving enameled
23 objects using laser beams by incorporating into the enamel
24 coating opacifying agents which the laser beam causes to
25 decompose optically and locally; for example, oxides of
26 titanium, tin, cerium, and antimony. A drawback of this
27 method is that, for example, transparent enameled objects
28 cannot be marked because the opacifying agent incorporated
29 in the enamel coating does not change optically at the non-
30 irradiated areas and, therefore, strongly influences the
31 overall appearance of the object. Furthermore, the
32 opacifying agent employed may adversely affect the
33 mechanical properties of the enamel.

1 Industry has sought to surface mark glass, ceramic,
2 porcelain, metal, plastics, and the like with four physical
3 attributes. These four attributes are high-resolution,
4 high-contrast, permanence, and speed.

5 Well known efforts to date have only produced two or
6 three of these attributes. For example, kiln marking
7 ceramics using glass frit material at kiln temperatures
8 ranging from 100° to 1000° C results in high-resolution,
9 high-contrast, permanent indicia on ceramics, glass, and
10 metals. These known processes require heating the entire
11 substrate along with the glass frit or metal oxide marking
12 material in a kiln. The problem with these processes is the
13 time factor and energy consumption are not commercially
14 efficient to create the indicia. Time factors ranging from
15 minutes to hours are common. Energy consumption of a kiln
16 is generally measured in kilowatts per ton and/or BTUs per
17 pound. Furthermore, these processes do not lend themselves
18 to portability.

19 Another known marking method is peening on metal. This
20 method cannot be used on glass, ceramic, or other brittle
21 materials because of surface damage and/or breakage. Where
22 used, this method produces a high-resolution, permanent,
23 fast surface indicia. However, high contrast marks are not
24 produced.

25 Other known marking methods are ink printing methods.
26 One state of the art transfer printing method is taught by
27 WO 95/13195 (May 1995) to Meneghine *et al*, assigned to
28 Markem Corporation. These methods use a laser-transferable
29 ink on a plastic carrier. The ink is mixed in a transfer
30 medium solution in order to enhance the conversion of laser
31 (IR) energy to heat. These methods produce a high-
32 resolution, high-contrast, and relatively fast method.
33 There is a UV cure step which is time consuming. The

1 problem with this and all ink methods is a lack of
2 permanence. Acids and other solvents remove ink from a hard
3 surface. This method teaches curing the ink onto the
4 substrate surface. *The present invention teaches bonding a*
5 *marking medium to form a new marking layer atop the*
6 *substrate surface rather than transferring an ink to the*
7 *substrate and then curing the ink.*

8 Another well known marking method teaches the use of
9 ink jet printers. In order to improve application
10 performance, appearance and permanence, environmentally
11 hazardous solvents are mixed with the ink. Even with these
12 hazardous solvents however, significant improvement has not
13 been achieved.

14 U.S. Pat. No. 4,541,340 (1985) to Peart et al.
15 discloses a printing process for marking fabrics or plastics
16 in a permanent image. Sublimable dyes are used such as
17 nitroso dyes. A diffusion of the dyestuff into the
18 substrate is caused by a pressurized air step on a transfer
19 label. Only application to fabrics and plastics is taught.
20 The chemistry is different from the present invention.
21 However, the result of a permanent high contrast mark is
22 claimed.

23 Another related group of marking methods is laser
24 combined with glass frit or metal oxide marking media. U.S.
25 Pat. No. 4,769,310 (1988) to Gugger et al. teaches first
26 creating a glaze in a kiln process. The glaze has a
27 radiation sensitive additive in amounts ranging from .01 to
28 30% by weight. This glaze is then irradiated by a beam of
29 Nd:YAG pulsed laser having light pulses of six to eight
30 nanoseconds at a wavelength of 0.532 μm and a pulse content
31 of 250 milli-joules. The problem with this method is the
32 burden of creating a time consuming glaze surface before
33 applying the high-speed laser beam.

1 U.S. Pat. No. 5,030,551 (1991) to Herren et al. teaches
2 a laser-based method to mark ceramic materials, glazes,
3 glass ceramics, and glasses by first applying to a workpiece
4 a 100 to 10,000 Angstrom thick transparent layer of titanium
5 dioxide. Second, the workpiece is fired in an oven at 620°
6 C for one minute and then slowly cooled in the closed oven.
7 Third, the layer is irradiated with a pulsed laser in
8 accordance with the form of the marking to be applied. The
9 laser light must have a wavelength which is sufficiently
10 absorbed by the oxide layer so that a discoloration of the
11 oxide layer is produced at the irradiated areas. The
12 problem with this method is the time and energy-consuming
13 step of firing and cooling the workpiece.

14 The method of the present invention makes it possible
15 to produce a direct and rapid marking that is indelible and
16 which is, therefore, abrasion and scratch-proof. The
17 markings obtained are also corrosion-proof, solvent-
18 resistant, dimensionally stable, free from deformation, fast
19 to light, heat, and weathering, easily legible, and have
20 good contrast and very good edge definition. In addition,
21 there is virtually no impairment of the mechanical,
22 physical, and chemical properties of the marked material,
23 e.g. mechanical strength and chemical resistance.

24 There has now been found a flexible method which makes
25 it possible to mark metals, plastics, ceramic materials,
26 glazes, glass ceramics and glasses without damaging the
27 surface thereof and without specific requirements being made
28 of the substrate, which method comprises the use of a glass
29 frit based or mixed organic materials or mixed metal oxide
30 layer for the laser marking.

31 Accordingly, the present invention relates to a method
32 of radiantly marking both conductive and dielectric
33 materials including metals, plastics, ceramic materials,

1 glazes, glass ceramics and glasses of any desired form which
2 comprises steps of applying to the substrate material a
3 marking material which, depending upon its principal
4 components, may or may not contain at least one energy
5 absorbing enhancer, then irradiating said marking material
6 layer with a laser or diode based energy source such that
7 the radiation is directed onto said layer in accordance with
8 the form of the marking to be applied, and using laser or
9 diode based energy of a wavelength which is sufficiently
10 absorbed by the marking material so that a bonding occurs on
11 the substrate, thereby forming a marking layer atop the
12 substrate.

13 A preferred embodiment of the present invention employs
14 electrostatic methods of applying marking materials to the
15 substrates. The principles behind electrostatics have been
16 applied in the development of electrophoresis, powder
17 coating sprayers, xerography and ink jet printers.
18 Electrostatic coating technology has been available for many
19 years and is widely used for the coating of household
20 appliances such as ranges, refrigerators, washing machines
21 and dryers. There are some subtle aspects to this science
22 such as fine atomizing of liquid droplets, fine de-
23 agglomerating and diffusion of powders, eliminating or
24 shielding unintended target areas, creation of an optimal
25 electrical charge on the part surface as well as optimizing
26 part geometry and orientation. Characteristics of
27 electrostatic coating processes include low energy
28 expenditure, absence of pollution or other undesirable
29 effluents, and high material utilization efficiencies. Its
30 applications reduce waste and improve manufacturing
31 efficiency and product quality. There are no apparent
32 adverse secondary effects from application of
33 electrostatics.

1 Behind the operation of all electrostatic coating
2 equipment is the fundamental principle that oppositely
3 charged bodies attract one another. Therefore, charged
4 marking material particles would be attracted towards a
5 grounded or oppositely-charged article. In the
6 electrostatic coating process, the target substrate is
7 grounded so that it is electrically neutral. The coating
8 system creates, electrically charges, and disperses solid
9 particles or liquid droplets of the marking material toward
10 the target substrate by a variety of methods well known to
11 one skilled in the art. The charged marking material
12 particles are attracted to the grounded, neutral substrate
13 and are deposited on it. Since the charged particles are
14 all charged alike they repel from each other during the
15 flight to the target and while "landing". These marking
16 material particles avoid each other and seek areas on the
17 target surface that are best grounded (i.e. uncoated areas).
18 This is one of the simplest and most elegant aspects of the
19 electrostatic coating process: deposition is uniform because
20 the least coated areas get coated by the "newest" particles.
21 The use of electrostatic deposition technology means that
22 very good reproducibility and precision of deposition can be
23 obtained - relative standard deviations (RSDs) of 1-2
24 percent of coating thickness can be achieved. This is a
25 significant improvement and tremendous advantage over
26 conventional coating methods.

27 Since the article being coated is the collecting
28 electrode in the electrostatic coating process, it should
29 have sufficient electrical conductivity, either through its
30 bulk or across its surface, to carry away the electrical
31 charge arriving on the surface with the accumulating marking
32 material particles. For this reason, the electrostatic

1 coating process is most often used to coat objects which are
2 natural conductors of electricity (e.g. metals).

3 Typically, such conductive articles are held at a
4 grounded potential by merely being supported from a grounded
5 conveyor with a metal hook. By induction from the charging
6 electrode, the conductive article assumes an electrical
7 charge, which is opposite to that of the charged marking
8 material particles. Accordingly, the electrically
9 conductive article attracts the charged marking material
10 particles.

11 Notwithstanding the above, electrostatic coating
12 practices are also used to coat articles made from non-
13 conductive or dielectric materials (e.g. plastics, glass,
14 ceramics, wood, etc.), hereinafter collectively referred to
15 as "dielectric materials". When used for these purposes, it
16 becomes necessary to make the dielectric material either a
17 permanent or temporary electrical conductor. A number of
18 techniques have been perfected to accomplish this objective
19 and these methods are well known to one skilled in the art.

20 For example, molded rubber steering wheels are not
21 natural conductors of electricity; however, they can be made
22 electrically conductive by heating them to temperatures of
23 at least about 212° F. (100° C.). While this practice works
24 well for electrostatically coating some dielectric
25 materials, it has a number of problems associated therewith.
26 For example, this practice cannot be used to induce a charge
27 on those dielectric materials which do not become
28 electrically conductive when heated (e.g., wood). Moreover,
29 this practice also cannot be used to induce a charge on
30 those dielectric materials, which begin to deform or degrade
31 at or below the temperature needed to make them electrically
32 conductive.

1 Another method of electrostatically spraying a
2 dielectric material consists of coating the material with an
3 electrically conductive primer. This practice is used in
4 the coating of toilet seats. Specifically, toilet seats are
5 normally made from a phenolic resin/wood-flour mixture.
6 This material is non-conductive and does not become
7 conductive upon heating. Accordingly, to make it possible
8 to electrostatically coat these items, the seats are first
9 sprayed with an electrically conductive, film forming
10 primer. When dried, this coating creates an electrically
11 conductive film on the surface of the seat. After being
12 coated with this primer, the seats are supported from a
13 grounded conveyor with metal hooks. Thereafter, the marking
14 materials could be electrostatically applied.

15 Electrostatic coating methods are disclosed in many
16 patents.

17 U.S. Pat. No. 2,622,833 discloses a process and
18 apparatus for electrostatically coating the exterior
19 surfaces of hollow articles made from a dielectric or non-
20 conductive material without the use of backing electrodes,
21 which conform to the shape of the article. In that patent,
22 the articles being coated are mounted onto spindles, which
23 are connected to a conveyor system. The conveyor and the
24 spindles are electrically conductive. Moreover, they are
25 both connected through a conductor to either a ground or a
26 power supply.

27 In U.S. Pat. No. 2,622,833, a conductive probe, which
28 has an ionizing point or points, is electrically connected
29 to the spindles. This probe is positioned so that it
30 passes, through the article's opening, into the cavity of
31 the article being coated. The spindles then carry these
32 articles between oppositely disposed, spaced negatively-
33 charged electrodes. As the articles pass the electrodes, an

1 electrostatic field is created between the negatively-
2 charged electrodes and the exterior surface of the article.
3 One or more spray guns are directed so as to introduce an
4 atomized coating composition in a direction generally
5 parallel to the path of travel of the articles into the
6 space between the articles and the electrodes. As the
7 marking material particles enter into the ionizing zone,
8 they accept a negative charge and are thus drawn to the
9 grounded or positively-charged article.

10 U.S. Pat. No. 4,099,486 also discloses a process and
11 apparatus for electrostatically coating glass bottles by
12 using a particular chuck for supporting the bottles which is
13 designed to prevent build-up of coatings thereon. That
14 patent induces a charge onto the glass bottles by heating
15 them to a temperature ranging between 150° F. (66° C.) to
16 450° F (232° C.). According to U.S. Pat. No. 4,099,486, the
17 supporting chuck is made from a non-conductive plastic.
18 This chuck fits over a grounding plug, which is designed to
19 ground the bottle by being in physical contact therewith.
20 For example, one embodiment of a ground plug described in
21 that patent is in the form of a flat-headed probe upon which
22 rests the neck of the bottle. Another embodiment of a
23 ground plug described in that patent is in the form of a
24 flat-ended rod which extends into the bottle's opening, and
25 through the bottle's entire length, until the distal end of
26 the rod contacts the inside surface of the bottle's base.
27 Yet another embodiment of a ground plug described in that
28 patent is in the form of a flat-ended rod whose outside
29 dimension is parallel to the inside dimension of the
30 bottle's opening. With this latter configuration, when the
31 ground plug is inserted into the bottle's opening, the
32 outside walls of the plug contact the inside walls of the

1 bottle's neck. Additional patents disclosing electrostatic
2 coating methods and apparatus include:

3 U.S. Pat. No. 6,063,194 (Dry Powder Deposition
4 Apparatus)

5 U.S. Pat. No. 5,830,274 (Electrostatic Deposition of
6 Charged Coating Particles onto a Dielectric Substrate)

7 U.S. Pat. No. 5,698,269 (Electrostatic Deposition of
8 Charged Coating Particles onto a Dielectric Substrate)

9 U.S. Pat. No. 4,099,486 (Electrostatically Coating
10 Hollow Glass Articles)

11 U.S. Pat. No. 4,110,486 (Electrostatic Powder Coating
12 Method)

13 U.S. Pat. No. 3,930,062 (Composition and Method for
14 Electrostatic Deposition of Dry Porcelain Enamel Frit)

15 U.S. Pat. No. 3,558,052 (Method and Apparatus for
16 Spraying Electrostatic Dry Powder).

17 Fully integrated electrostatic coating systems are
18 commercially available for efficient coating of small parts
19 in laboratory and batch-production operations from companies
20 such as Trutec Industries, Powder Spray Technologies, Double
21 D Equipment Company and Wagner International. To coat small
22 parts, use of an electrostatic or hot-dip fluidized bed
23 system can provide efficient coating quality. An
24 electrostatic fluidized bed can be used for either
25 electrostatic deposition or for hot-dip coating of small
26 parts, and can operate with just a few ounces of marking
27 materials.

28

29 SUMMARY OF THE INVENTION

30 The main aspect of the present invention is to provide
31 a method to quickly, with high-resolution, high-contrast,
32 and permanence, mark the surface of a workpiece.

1 Another aspect of the present invention is to provide a
2 method to irradiate a marking material which may or may not
3 contain at least one energy absorbing enhancer, wherein the
4 marking material is selected from the group consisting of
5 glass frits, glass frits with ceramic colorants, and glass
6 frits with porcelain enamels, where the workpiece is a
7 conductive or dielectric material such as glass, ceramic,
8 porcelain, certain metals, and certain plastics. (Clear
9 glass and glass frits do not absorb energy in the 1 micron
10 range of the Nd:YAG or diode lasers, but do absorb energy in
11 the 10 micron range, so these materials may not require
12 additional energy absorbing enhancers.)

13 Another aspect of the present invention is to provide a
14 method to irradiate a marking material containing metal
15 compounds including mixed metal oxides where the workpiece
16 is metal, glass, ceramic, porcelain and certain plastics.

17 Another aspect of the present invention is to provide a
18 method to irradiate a marking material containing mixed
19 organic pigments where the workpiece is plastic, glass,
20 ceramic, porcelain and certain metals.

21 Another main aspect of the invention related to all of
22 the above aspects is to provide various electrostatic
23 methods of applying the marking materials to the substrate
24 to be marked.

25 Other aspects of this invention will appear from the
26 following description and appended claims, reference being
27 made to the accompanying drawing forming a part of this
28 specification wherein like referenced characters designate
29 corresponding parts in the drawing.

30 Thus, in accordance with the present invention, a
31 series of thermally activated, chemically based marking
32 methods are provided, comprising steps of:

1 electrostatically applying a layer of an energy
2 absorbing marking material to a conductive or dielectric
3 substrate to be marked; and

4 irradiating the layer of marking material with a
5 radiant energy beam having a wavelength selected to excite
6 the energy absorbing material in accordance with the form of
7 a marking to be applied, thereby forming a marking layer
8 atop the substrate. The objective is generally to provide a
9 bonded and permanent marking atop the substrate which is
10 visible in contrast with the substrate.

11 When electrostatically applying the marking material to
12 dielectric substrates, a conductive layer of material is
13 normally first applied to the substrate.

14 The irradiation process can be improved by providing a
15 laminar air flow across the substrate during the irradiating
16 step which maintains a consistent environment by carrying
17 away any gasses created during the irradiating step of the
18 inventive process, and preferably is started at an ambient
19 temperature of about 70 deg. F.

20 The marking material can comprise a variety of
21 substances which can be tailored to the substrate, but must
22 contain at least one component which will absorb sufficient
23 radiant energy to cause the marking material to fuse or
24 sinter and create a permanently bonded marking upon the
25 substrate. In some cases an energy absorbing enhancer such
26 as carbon black can be included in the marking material.
27 The marking materials can include various metal compounds
28 including oxides, mixed oxides, sulfides, sulfates,
29 carbonates, carbides, nitrides and silicides. Colorants can
30 be included, as described below. The marking material can
31 also include various types of glass frit material, alone or
32 in combination with various metal compounds.

1 The substrates can comprise a variety of conductive and
2 dielectric materials selected from suitable metals, glasses,
3 ceramics and plastics.

4 Prior to the present invention, no quick and permanent
5 method existed for marking certain substrate materials with
6 enhanced contrast and/or color which would also permit the
7 rapid change of content and/or information in the mark
8 without structural damage to the substrate material. In
9 theory, an optical power source, properly focused, could
10 create the same temperatures obtained by ovens and/or kilns
11 used in conventional "firing" processes involving marking
12 materials. The speed of computer controls for the optical
13 power source, the beam steering mechanism and the mark
14 content make it possible for individual enhanced contrast
15 and/or color marks to be bonded to the various substrate
16 materials in extremely short time periods without structural
17 damage in a way not attainable by any other marking or
18 decorating process. The wide variety of marking materials
19 make it possible to produce images with varying optical
20 properties including, but not limited to, contrast, color,
21 reflectance, diffraction; and varying physical properties
22 including, but not limited to, thickness, durability,
23 stability, structural shape and electrical conductivity.

24 The present inventive process of permanently marking
25 materials will be especially useful in marking glass,
26 ceramic, porcelain, and other brittle materials whose
27 surface structure cannot withstand the thermal shock of
28 other commonly used high-power pulsed laser marking methods.
29 In the present invention, the resulting images on all
30 substrate materials have enhanced contrast and/or color
31 which makes the mark more easily viewed and imaged by the
32 human eye and/or machine vision equipment and is highly
33 resistant to chemical and mechanical wear. This feature is

1 a great advance in barcode and 2D symbology marking, since
2 the prior art high-power pulsed laser-only marking systems
3 cannot always create sufficient contrast and/or color
4 markings.

5 This invention relates to the permanent bonding of
6 enhanced contrast and/or colored materials to the surfaces
7 of various conductive or dielectric materials including
8 glass, ceramic, porcelain, metal, and plastic substrates
9 using radiant energy produced by, but not limited to,
10 optical power sources such as lasers, laser diodes, direct
11 diodes and diode-pumped lasers. The sun's radiant energy,
12 properly filtered and focused, could make an acceptable
13 radiant energy source. The wavelength (λ) and output power
14 (watts) of the optical power source are determined by the
15 combination of the composition of the substrate material and
16 the natural or enhanced energy absorbing characteristics of
17 specific marking material to be applied. The marking
18 materials are formulated to react with various substrate
19 materials at certain temperatures. The radiant energy
20 source can produce the required temperatures in small
21 localized areas within microseconds and create an
22 environment where the desired chemical and mechanical
23 reactions will occur. Virtually any computer-generated mark
24 can be produced on a substrate by moving the beam emanating
25 from the radiant energy source on the marking material on
26 the surface of the workpiece using conventional beam
27 steering mechanisms and/or X - Y plotter mechanisms and/or
28 by moving the workpiece relative to a stationary beam.

29 The marking material is electrostatically applied to
30 the surface of the workpiece. The beam emanating from the
31 radiant energy source impinges upon the marking material,
32 which absorbs the radiant energy and elevates it to the
33 required temperature. In absorbing the radiant energy, at

1 least a portion of the marking material is excited, i.e. has
2 its atoms or molecules raised to an excited state. [See
3 Webster's Encyclopedic Unabridged Dictionary of the English
4 Language (Portland House, New York, 1989), page 497.]
5 Typically , a temperature of 200° to 1500° F is reached in
6 approximately one to two microseconds. Precise temperatures
7 are controlled by the output power of the radiant energy
8 source and the physical position of the marking material
9 relative to the focal plane of the radiant energy beam and
10 the speed with which the beam is moving. Once the required
11 temperature is achieved, the marking material and substrate
12 will permanently bond together to form a new marking layer
13 atop the substrate. The interaction of the radiant energy
14 and the marking material is believed to result in an inert
15 coating mechanically and chemically bonded to the substrate
16 material. The marking layer is believed to form covalent
17 bonds with the substrate material, and it is believed this
18 chemical bond exceeds the strength of the mechanical bond.
19 Marking materials can be formulated to absorb specific
20 amounts of a specified wavelength of the radiant energy.

21 CO₂ lasers are capable of permanently marking glass
22 materials by thermally shocking the surface and causing
23 fractured facets. These fractures are detrimental to the
24 structural integrity of the glass and will continue to
25 propagate, causing chips to fall out of the mark.
26 Furthermore, the imaged mark has no enhanced contrast and is
27 difficult to view or image. Certain organic materials
28 (wood, plastic, etc.) are easily marked using CO₂ lasers,
29 but the resulting imaged mark can only have limited color
30 and/or contrast based on the material composition and the
31 effect of the laser energy (it will cause burning of the
32 surface). There are a number of specially formulated

1 plastic materials that will change color when exposed to
2 specific laser energy and produce an enhanced contrast mark.

3 Nd:YAG lasers are generally capable of permanently
4 marking a variety of metals and some organic materials.
5 However, the same limited variation of color and contrast
6 applies. Some steels and other hard metals can be burned
7 with sufficient laser power to produce a dark mark against
8 the natural surface color. However, the heat created by
9 this method causes the area surrounding the mark to darken
10 resulting in significantly decreased contrast.
11 Additionally, very few color variations are possible. Most
12 direct diodes cannot produce sufficient beam quality or
13 power to achieve the same effects as the Nd:YAG lasers.

14 The principal advantages of the inventive process are:

- 15 - no structural damage to the substrate material
16 surface;
- 17 - no post processing required to stabilize the
18 finished mark;
- 19 - wide variety of colors, contrasts and physical
20 properties;
- 21 - high resolution for the imaged mark;
- 22 - resistant to chemical and mechanical wear;
- 23 - marking speeds in seconds, not minutes or hours;
- 24 - image content can be changed at computer speeds;
- 25 - individual marks can be fully automated; and
- 26 - permanent markings will withstand flexing,
27 expansion and contraction of substrate.

28 Features of the inventive process believed to be
29 significant improvements are:

- 30 1) The use of laser or diode based radiation to
31 rapidly elevate the temperature of the marking
32 material atop the substrate to form a new marking
33 layer atop the substrate.

1 2) a single laser beam pass is all that is required.

2 3) Selecting marking materials specially formulated

3 to react with specific substrate materials using

4 laser or diode based radiation as the catalyst.

5 4) Speed with which the mark can be produced.

6 5) Speed with which the content of the mark can be

7 changed.

8 6) Method of delivery of marking material to the

9 substrate surface including various types of

10 electrostatic deposition.

11 7) Marks can be applied to glass and other brittle

12 surfaces without fracturing.

13 8) Enhanced contrast and/or color of mark.

14 9) Two-, three-, or four-color images can be marked

15 with near photo quality.

16 10) Elimination of any firing step of entire

17 workpiece.

18 11) Ability to first ablate (if desired) and then mark

19 selected substrates to create 3D high-contrast

20 markings with a simple two-step process.

21 12) Using relatively low-cost, low-contaminating

22 marking materials (glass frits, mixed metal

23 oxides, or mixed organic pigments) instead of

24 silver oxides or other high-cost highly-toxic

25 materials.

26 13) Higher resolution of imaged mark (>1000 dpi).

27

28 A significant feature added by the present invention is

29 the use of various suitable electrostatic methods of

30 applying the marking materials to the substrates be

31 radiantly marked using radiant energy. As described above

32 in general and below in detail as to the present invention,

33 many electrostatic application methods are known to those in

1 the art, and suitable disclosures are found in many U.S.
2 patents. In most cases where marking materials are to be
3 applied to conductive materials such as metals, the marking
4 materials can be directly applied in liquid, aerosol or
5 finely-divided solid form to the substrate or other surface
6 to be marked by suitable electrostatic methods. When
7 dielectric materials such as glasses, ceramics, plastics and
8 the like are to be marked, a conductive coating or layer
9 should normally be applied to the surface before the marking
10 materials themselves are electrostatically applied, as is
11 well known in the art.

12 A more complete appreciation of the present invention,
13 and many of the attendant aspects and advantages thereof,
14 will be readily ascertained as the invention becomes better
15 understood by reference to the following Detailed
16 Description when considered with the accompanying Figures
17 briefly described below.

18

19 **BRIEF DESCRIPTION OF FIGURES AND EXAMPLES**

20 The following figures are incorporated by reference from
21 the parent application, U.S. Serial No. 08/925,031, filed
22 September 8, 1997 and issued as U.S. Pat. No. 6,075,223 on
23 June 13, 2000, with FIG. 1 of that application omitted.

24 In all the below listed figures, the resulting marks
25 were produced on commercially available Nd:YAG laser markers
26 as manufactured, for example, by GSILumonics Corporation, A
27 B Lasers, Inc., Control Laser, Inc., and/or Rofin Sinar,
28 Inc. with power capability and optical configurations
29 capable of providing the referenced marker parameters. In
30 all examples the laser marker utilized produced a spot size
31 of 100 to 125 microns, and the surface of the workpiece was
32 placed 2mm to 3mm below the focal plane of the laser beam.
33 In FIG. 1 through FIG. 7 the marking material was applied

1 with resulting thicknesses between 75 and 125 microns on the
2 workpiece surface.

3 FIG. 1 is a photograph of a stainless steel workpiece
4 having the uppermost mark produced using Cerdec 29-1777
5 Amber Stain mixed metal oxide mixed at a 1/1 ratio by weight
6 with mineral oil as the marking material with the inventive
7 process and exhibiting high contrast from all viewing angles
8 with no detectable damage to the workpiece surface. The mark
9 was produced using 5 watts of CW energy at a beam speed of
10 200mm/second. The lower mark was produced using the same
11 laser settings without the inventive process resulting in
12 only an ablative laser process and a mark of varying
13 contrast that is totally dependent upon the viewing angle.

14 FIG. 2 is a photograph of a polished stainless steel
15 workpiece having the mark produced using Cerdec 29-1777
16 mixed metal oxide mixed at a 1/1 ratio by weight with
17 mineral oil as the marking material with the inventive
18 process and exhibiting high contrast from all viewing angles
19 with no detectable damage to the workpiece surface. The mark
20 was produced using 5 watts of CW energy at a beam speed of
21 200mm/second.

22 FIG. 3 is a photograph of an aluminum workpiece having
23 the mark produced using 10 parts Cerdec 29-1060 mixed metal
24 oxide combined with 1 part Cerdec 29-1777 mixed metal oxide
25 and then mixed at a 1/1 ratio by weight with mineral oil as
26 the marking material with the inventive process and
27 exhibiting high contrast from all viewing angles with no
28 detectable damage to the workpiece surface. The mark was
29 produced using 5 watts of CW energy at a beam speed of
30 200mm/second.

31 FIG. 4 is a photograph of an alumina ceramic workpiece
32 having the mark produced using Cerdec 24-2702 glass frit
33 containing energy absorbing enhancers mixed at a 1/1 ratio

1 by weight with mineral oil as the marking material with the
2 inventive process and exhibiting high contrast from all
3 viewing angles with no detectable damage to the workpiece
4 surface. The mark was produced using 5 watts of CW energy at
5 a beam speed of 200mm/second.

6 FIG. 5 is a photograph of a quartz-glass light bulb
7 having the mark produced using Cerdec 24-2702 glass frit
8 containing energy absorbing enhancers mixed at a 1/1 ratio
9 by weight with mineral oil as the marking material with the
10 inventive process and exhibiting high contrast from all
11 viewing angles with no detectable damage to the workpiece
12 surface. The mark was produced using 5 watts of CW energy at
13 a beam speed of 200mm/second.

14 FIG. 6 is a photograph of a soda-lime glass microscope
15 slide having the mark produced using Cerdec 24-2702 glass
16 frit containing energy absorbing enhancers mixed at a 1/1
17 ratio by weight with mineral oil as the marking material
18 with the inventive process to form a 2D symbology mark with
19 alpha-numeric characters and exhibiting high contrast from
20 all viewing angles with no detectable damage to the
21 workpiece surface. The mark was produced using 5 watts of CW
22 energy at a beam speed of 200mm/second.

23 FIG. 7 is a photograph of a piece of borosilicate flat
24 panel display glass having the mark produced using Cerdec
25 24-2702 glass frit containing energy absorbing enhancers
26 mixed at a 1/1 ratio by weight with mineral oil as the
27 marking material with the inventive process to form a 2D
28 symbology mark with alpha-numeric characters and exhibiting
29 high contrast from all viewing angles with no detectable
30 damage to the workpiece surface. The mark was produced using
31 5 watts of CW energy at a beam speed of 200mm/second.

32 FIG. 8 is a chart showing the laser marker parameters
33 used to produce marks on a variety of substrate materials.

1 FIG. 9 is a drawing of the inventive process in action.
2 FIGS. 10a through 10d show a 2D profile of a small
3 portion of the mark produced with the inventive process as
4 shown in FIG. 6 with an average thickness of approximately 3
5 microns and a maximum thickness of approximately 14 microns.
6 Similar results are obtained when using the inventive
7 process on other substrate materials.

8 Hypothetical Example A

9 The marking materials and substrate described and
10 illustrated in FIG. 1 above are employed, applying the
11 marking materials electrostatically as dry particles.
12 Application of the same laser beam producers markings which
13 have more even edges, a smoother surface and more uniform
14 thickness.

15 Hypothetical Example B

16 The marking materials and substrate described and
17 illustrated in FIG. 1 above are employed, applying the
18 marking materials electrostatically as liquid droplets.
19 Application of the same laser beam producers markings which
20 have more even edges, a smoother surface and more uniform
21 thickness.

22 Hypothetical Example C

23 The marking materials and substrate described and
24 illustrated in FIG. 5 above are employed, applying the
25 marking materials electrostatically as dry particles.
26 Application of the same laser beam producers markings which
27 have more even edges, a smoother surface and more uniform
28 thickness.

29 Hypothetical Example D

30 The marking materials and substrate described and
31 illustrated in FIG. 5 above are employed, applying the
32 marking materials electrostatically as liquid droplets.
33 Application of the same laser beam producers markings which

1 have more even edges, a smoother surface and more uniform
2 thickness.

3 Before explaining the disclosed embodiment of the
4 present invention in detail, it is to be understood that the
5 invention is not limited in its application to the details
6 of the particular arrangement shown, since the invention is
7 capable of other embodiments. Also, the terminology used
8 herein is for the purpose of description and not of
9 limitation.

10

11 **DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS**

12 Below follow some basic definitions as used herein:

13 Ceramic and porcelain enamel: A soft melting glass
14 similar in all cases and like other ceramic glazes, composed
15 of fluxes and alumino-silicates. Porcelain enamels are
16 typically used on metallic surfaces.

17 Glass frits: Pre-fused glass material which is
18 produced by fritting (the rapid chilling of the molten
19 glassy material), then ground to a powder. Frits are
20 typically employed as a constituent in a glaze.

21 Mixed metal oxides: An oxide compound containing more
22 than one metal oxide.

23 Glass frits generally are composed of alkali metal
24 oxides, alkaline earth metal oxides, silica, boric oxide and
25 transition metal oxides. In specific, additional
26 information is known about the commercial marking materials
27 Cerdec 29-1060 Amber stain, which contains silver sulfide,
28 copper, copper oxide, barium sulfate, iron sulfide, calcium
29 hydroxide and crystalline silica. Also, Cerdec 29-1777
30 Amber stain is also known to contain silver sulfide, copper
31 oxide, copper-iron sulfide and kaolin clay. Also, Cerdec
32 29-346 Amber stain is known to contain copper, copper oxide,
33 silver sulfide, barium sulfate, iron sulfate, iron oxide,

1 and crystalline silica. Also, Cerdec 24-2702 black stain is
2 known to contain lead borosilicate frit, C.I. pigment black
3 27 (containing cobalt compounds, iron oxide chromium
4 compound), C.I. pigment black 30 (containing nickel,
5 manganese and chromium compounds and iron oxide) C.I.
6 pigment blue 72 (containing cobalt compound).

7 Comparable mixed metal oxide and glass frit materials
8 can be secured through manufacturers such as Bayer Company,
9 Cookson Matthey Zircon, Ferro Corp., Cerdec Corp., E.I.
10 duPont de Nemours & Co., Hoechst Celanese Corp., and Dow
11 Chemical Co.

12 The method of this invention is especially suitable for
13 marking metals, plastics, glasses, and glass ceramics.
14 Glasses and glass ceramics are well known to the person
15 skilled in the art and described, for example, in Ullmanns
16 Enzyklopädie der technischen Chemie, 4th edition, Vol. 12,
17 pp. 317-366.

18 By ceramic materials are meant inorganic, non-metallic,
19 high-melting materials that are usually referred to in the
20 literature as clay ceramics and special ceramics. Examples
21 thereof are oxides in crystalline or glassy form, e.g.
22 alkali metal or alkaline earth metal aluminosilicates or
23 aluminoborates, as well as non-oxides such as carbides,
24 nitrides, and silicides. For further examples, attention is
25 drawn to Ullmanns Enzyklopädie der techn. Chemie, 4th
26 Edition, Vol. 13, pp. 712-716.

27 Glazes are classified chemically as follows:

- 28 1. Bases, the conspicuously fluxing agents,
29 represented by alkali metal oxides, the alkaline
30 earth oxides, zinc oxide, lead oxide and many
31 coloring oxides or chromophoers.
- 32 2. Intermediates, which includes amphoteric oxides, a
33 group from which alumina is the common example and

1 to which ferric, chromic, manganic, and other
2 oxides are sometimes assigned. Boric acid is
3 sometimes considered a member of this group.

4 3. Acids, to which silica, phosphoric oxide, zirconia
5 and fluorine belong.

6 Glazes are glassy coatings applied to a ceramic
7 material and having a composition very similar to that of
8 glass (op. Cit., pp. 722-724). Typical examples of glazes
9 are those containing quartz, clay, alkali metal oxides,
10 alkaline earth metal oxides, and low-melting oxides (such as
11 Na₂O, K₂O, CaO, BaO, and PbO) as fluxes.

12 The elements listed on the far left of the Periodic
13 Table (as now drawn up and widely circulated) are all
14 elements that form Bases when their oxides are combined with
15 water, eg, Na₂O + H₂O = 2NaOH (lye). So do lime (CaO) and
16 magnesia (MgO). The elements at the right, the non-metals
17 mostly, form Acids when their oxides combine with water, eg,
18 CO₂ + H₂O = H₂CO₃, (carbonic acid). The elements in between,
19 mostly "transition metals", tend to exhibit "amphoteric"
20 behavior, i.e., they can go either way, depending what else
21 is close by.

22 A molten glass is chiefly a network made up of silicon
23 oxide molecules linked together in chains. But at very high
24 temperature, the silica molecules are free to roam around,
25 and in a sense behave as a solvent of other molecules.
26 Alumina (Al₂O₃) dissolves in this solvent and the combination
27 is "acidic"; if the molten glaze contains lesser amounts of
28 basic molecules (the oxides of the alkali metals and the
29 alkaline earth elements in particular), the glaze will be
30 classifiable as an acidic glaze, and copper oxide will
31 impart a green colour to the glaze on cooling (oxidation
32 conditions only). If, however, there are sufficient
33 molecules of the basic elements in the mix, the glaze will

1 be said to be basic and in it copper oxide will exhibit a
2 blue colour (e.g., soda blue of raku).

3 Depending on the utility, the materials to be marked
4 may be colorless, white, black or colored with a suitable
5 pigment on which the resulting marking layer additionally
6 provides contrast or which contains a pigment (e.g. metal,
7 glass, ceramic or organic colorant).

8 In the practice of this invention, the laser or diode
9 utilized must provide a relatively low energy level ranging
10 from 1 to 20 watts at the workpiece surface to be marked.
11 Commercially available and conventionally powered laser
12 marking systems operating in either continuous wave or
13 pulsed mode can be used. For example, a pulsed, Nd:YAG
14 laser with a maximum capacity of 100 watts and pulse
15 durations of 5 to 200 microseconds at a frequency of 20 kHz
16 or higher could be used. However, use of this type of laser
17 would require reducing the effect of the radiant energy
18 using mechanical apertures and/or neutral density filters
19 and/or polarizers and/or de-focusing the beam at the surface
20 of the workpiece as shown in FIG. 9.

21 The workpiece illustrated in FIG. 6 was created using a
22 Lumonics Lightwriter™ lamp pumped Nd:YAG laser marker
23 configured with a 2mm mechanical aperture and a polarizer
24 which produced a CW beam focused by a 100mm by 100mm flat
25 field lens to a spot size of approximately 125 microns with
26 measured power of 5 watts and which was moved by a beam
27 steering mechanism at a speed of 200mm/second.

28 Additionally, a Uniphase Stablite™ diode pumped Nd:YAG
29 laser has been used which produced a 700 micron diameter CW
30 beam focused using a 50mm lens to a spot size of 90 microns
31 with measured power of 3.1 watts and moved manually at a
32 speed of approximately 50mm/second.

1 In FIG. 9, the conventionally powered laser beam 100,
2 105 is de-focused at the surface 109 of the workpiece 106 by
3 allowing the laser beam 100 to pass through the focal plane
4 102 and impinge upon the marking material 103 applied to the
5 surface 109 of the workpiece 106. It has been shown that
6 placing the workpiece as shown below the focal plane using
7 the diverging radiant energy 105 is preferred over the use
8 of the converging radiant energy 100 above the focal plane
9 102. The resulting spot 104 has a diameter d_1 in the
10 preferred mode of 5 to 200 microns. The direction of
11 movement 108 of the diverging laser beam 105 on the surface
12 of the marking material 103 is shown. A beam steering
13 mechanism 110 moves the beam. The resulting bonded layer
14 comprising the mark 107 is shown in contrast to the
15 remaining non-irradiated marking material 103 on the surface
16 109 of the workpiece 106.

17 In a preferred embodiment of this invention, a less
18 expensive, less powerful air-cooled laser which consumes
19 considerably less electric energy, such as a direct diode or
20 diode pumped laser is used. Optimal results are generally
21 obtained using 5 watts of average power with a spot size of
22 125 microns moving at a speed of 200mm/sec across the
23 surface of the marking material.

24 Lasers whose parameters can be readily adjusted, for
25 example, pulse content and pulse duration, permit the best
26 possible adaptation to the requirements of the marking
27 material 103 and the composition of workpiece 106 to be
28 marked. In no case is a preheating of the workpiece 106
29 necessary. The proper radiant energy is that at which the
30 marking material absorbs energy most efficiently. It is a
31 major advantage of the present invention that only a single
32 pass of the irradiating beam is required to practice the
33 invention. In all experiments the inventive process was

1 practiced at a room temperature of approximately 70° F.
2 Furthermore, it is believed that both hot and cold substrate
3 materials can be marked during their production using the
4 inventive process.

5 In an alternate embodiment of the invention, the
6 workpiece may be moved under a stationary laser beam at
7 similar relative speeds to produce the desired mark.

8 Preferably, the relative speeds taught herein are
9 executed by the use of a computer controlled workpiece
10 movement mechanism (not shown) for example, an X-Y and/or
11 rotary stage using stepper and/or servo motors as supplied
12 by Newport Corporation and/or a beam steering mechanism (not
13 shown) for example the HPM™ Scan Head using galvo-mirrors
14 as supplied by General Scanning, Inc. Alternately, beam
15 steering can be effected, for example, acousto-optically,
16 holographically, or by polygon scanners.

17 Some suitable combinations of marking materials and
18 workpiece composition are listed below:
19

20 **TABLE I**

<u>Marking Materials</u>	<u>Substrate Materials</u>
22 1. Glass frit with energy 23 absorbing enhancers and 24 certain colorants and/or 25 pigments including por- 26 celain enamels	Glass, ceramic, porcelain and certain metals including aluminum, brass steel and stainless steel
28 2. Mixed metal oxides with 29 energy absorbing enhancers 30 and certain colorants and/ 31 or pigments	Metals including aluminum brass copper, nickel, tin steel, stainless steel, and certain glasses, ceramics and plastics

3. Mixed organic pigments with energy absorbing enhancers Commercial plastics including ABS, PVC, Nylon™, Delrin™ Teflon™ and Plexiglas™

7 Use of and/or the combination of different compositions
8 of marking material, second and/or subsequent applications
9 of marking material and/or the adjustment of laser
10 parameters will result in variations in the durability,
11 appearance, and structural form of the resulting mark.
12 Thus, a person skilled in the art of laser marking can
13 create a wide variety of marking characteristics to suit his
14 requirements. All of these marking characteristics can be
15 achieved with the use of a single low-power, low-cost air-
16 cooled diode laser. Furthermore, an infinite variety of
17 colors can be achieved. These features are a significant
18 advance in the art of surface marking.

Preparation of the marking materials, in liquid form, can, for example, occur through low shear mechanical mixing, high shear mechanical mixing, ultrasonic mixing and/or milling. The marking material, in liquid form, can be manually or automatically applied to the substrate surface at the desired thickness by hand-spraying it onto the substrate surface using automated electrostatic spray equipment. Excess material not bonded to the substrate surface can be removed by conventional cleaning processes. In high-volume applications, the unused marking material can be recovered from the cleaning process and reused.

30 Electrostatic application of marking materials in
31 liquid and/or aerosol form can be carried out using suitable
32 electrostatic methods known in the art, according to the
33 types of substrates to be marked, as discussed above.

1 Different techniques will be appropriate for applying
2 marking materials to conductive, dielectric or semiconductor
3 materials.

4 The present invention relates to a method for coating
5 objects by electrostatic powder-coating, according to which
6 the dry powder particles or liquid droplets are mixed with a
7 transporting gas and converted into a fan-shaped spray
8 before reaching the object to be coated. In the technique
9 of electrostatic coating, as was emphasized in the U.S. Pat.
10 No. 3,263,127 (which is incorporated herein by reference), a
11 fan-spray is of particular interest since the dry powder
12 particles or liquid droplets, thanks to the fan shape, may
13 be more easily charged by ion bombardment. Since the duct
14 carrying the "transporting gas" mixture to the gun is
15 cylindrical and of small diameter (in general, 7 to 10
16 millimeters), it is not easy to change such a cylindrical
17 stream into a homogeneous fan-spray several centimeters
18 wide. Shaping the stream by simply transforming the shape
19 of the duct, as shown in U.S. Pat. No. 3,263,127, is not
20 entirely satisfactory, as the spray obtained is bound to
21 lack homogeneity on account of the high degree of mechanical
22 inertia of the dry powder particles or liquid droplets, the
23 majority of which tend to come out through the center of the
24 outlet slit, while very few emerge at its edges. Moreover,
25 if such a nozzle is placed with the fan-spray in a vertical
26 position, experience shows that due to the effect of gravity
27 most of the powder particles come out toward the bottom of
28 the slit.

29 To overcome these drawbacks, there has already been
30 suggested, as described in U.S. Pat. No. 3,870,232 (which is
31 incorporated herein by reference), a nozzle equipped with
32 separate outlet tubes, the dry powder particles or liquid
33 droplets being sucked into each of them by means of

1 auxiliary air being injected through holes of a given
2 diameter, which produces perfect homogeneity of the total
3 spray, whatever the angle of the nozzle. Such a nozzle
4 functions with a strong air flow, which is advantageous in
5 certain cases, for example when it is wished to coat at a
6 distance, but which is often not desired, since a powerful
7 air flow may prevent the marking material from being
8 deposited on certain shapes of objects, due to a blowing
9 effect. Finally, it is well known that greater electrostatic
10 efficiency is obtained when the dry powder particles or
11 liquid droplets are slowed down as they leave the nozzle,
12 thus enabling them to follow the lines of force of the
13 electric field more easily; a strong axial air flow,
14 however, increases the axial speed of the stream.

15 The process, as described in U.S. Pat. No. 4,110,486
16 (which is incorporated herein by reference), makes it
17 possible to overcome the drawbacks of the previous systems,
18 and so to produce an electrostatic spraying nozzle which
19 provides at its outlet a fan-spray of dry powder particles
20 or liquid droplets, the contents of said spray being
21 homogeneous whatever its angle may be, and its speed being
22 slow compared with the speed of the incident "transporting
23 gas" mixture. It will be appreciated that the marking
24 material is uniformly suspended in the "transporting gas"
25 when it leaves the extraction device. If the speed of the
26 stream of "transporting gas" is high, that is to say greater
27 than about 15 meters/second, and there are no substantial
28 bends in the passage leading from the extraction device to
29 the nozzle, the marking material will remain homogeneously
30 distributed throughout the "transporting gas" stream
31 resulting in a uniform application of the marking material
32 onto the substrate surface.

Electrostatic Marking Materials

Dry nonconductive powder passes from a hopper by means of a vibrating plate through an adjustable, nonclogging extraction device and is directed by means of a stream of "transporting gas" issuing through a rectangular orifice from a variable volume plenum chamber into a venturi. The marking material passes into the venturi and from the venturi through a discharge nozzle and from the discharge nozzle onto the substrate to be coated. Corona wires are located in the proximity of the issuing end of the discharge nozzle so as to charge the dry powder particles or liquid droplets in order to direct them onto the substrate.

14 A composition for electrostatic deposition of dry
15 porcelain enamel frit wherein the frit is reacted with a
16 flow improving additive containing of an alkoxy silane, and
17 preferably combined with an adhesion promoting composition
18 consisting of a silazane is disclosed in U.S. Pat. No.
19 3,930,062. Additional benefits are also derived if the
20 sprayed composition also includes a chlorosilane.

21 In support of this disclosure, the following U.S.
22 Patents are incorporated herein by reference in their
23 entirety:

24 U.S. 5,698,269 (Electrostatic Deposition of Charged
25 Coating Particles onto a Dielectric Substrate)

26 U.S. 5,830,274 (Electrostatic Deposition of Charged
27 Coating Particles onto a dielectric Substrate)

28 U.S. 4,099,486 (Electrostatically Coating Hollow Glass
29 Articles)

30 U.S. 3,930,062 (Composition and Method for
31 Electrostatic Deposition of "Dry Porcelain enamel Frit")

1 U.S. 3,558,052 (Method and Apparatus for Spraying
2 Electrostatic Dry Powder)

3 U.S. 4,110,486 (Electrostatic Powder Coating Method)

4 U.S. 6,063,194 (Dry Powder Deposition Apparatus)

5 6,202,945 (Method and apparatus for electrostatic
6 powder coating)

7 5,925,419 (Electrostatic powder coating method for road
8 wheels)

9 5,915,621 (Electrostatic powder coating method and
10 apparatus)

11 5,811,158 (Method and apparatus for electrostatic
12 powder coating)

13 5,776,554 (Electrostatic powder coating system and
14 method)

15 5,747,150 (Electrostatic powder coating method)

16 5,711,489 (Electrostatic powder coating method and
17 apparatus)

18 5,695,826 (Electrostatic powder coating apparatus and
19 method)

20 A laminar air flow across the surface of the workpiece
21 is created by venting and/or exhausting equipment insuring a
22 consistent localized environment in which the inventive
23 process can occur.

24

1

2 **Marking Materials**

3 Generally, the marking materials useful in the
4 invention comprise a wide variety of components which can be
5 used alone or in combination to absorb radiant energy,
6 create heat and form (through fusing, sintering or the like)
7 a permanent marking upon a substrate. As discussed
8 elsewhere in this application, the nature of the substrate,
9 the radiant energy source and the components to be used in
10 the marking material must be selected with regard to how
11 they will function together. The finished markings may be
12 visible and/or colored, but may also be invisible under
13 normal light, but visible in other parts of the spectrum
14 such as the IR or UV ranges, and can also be fluorescent
15 and/or luminous.

16 The marking materials may be specifically described as
17 those materials which, upon application of sufficient laser
18 or diode based energy to produce the necessary heat, bond to
19 glass or ceramic or other substrates to provide an enhanced
20 contrast and/or color marking on the substrate. Low
21 temperature glass frits and the like can be used alone or in
22 combination with other materials.

23 A wide variety of metal compounds can be used as
24 components of the marking material, generally selected from
25 the oxides, mixed oxides, sulfides, sulfates, carbonates,
26 carbides, nitrides, silicides, and hydroxides of the alkali
27 metals, alkaline earth metals and transition metals. Such
28 compounds can be used to perform at least one function such
29 as absorbing the radiant energy, fusing and/or sintering to
30 form a bond with the substrate.

31 Representative metals and metal compounds which are
32 expected to be useful include copper, copper oxides, silver
33 sulfide, iron oxides, iron sulfide, iron sulfate, barium

1 sulfate, calcium hydroxide, copper-iron sulfides, silica,
2 various cobalt compounds and iron-chromium oxides.

3 Examples of suitable inorganic pigments which might be
4 used are described in Ullmanns Enzyklopädie der techn.
5 Chemie, 4th Edition, Vol. 14, pp. 1-12, and in the
6 publication of the Dry Color Manufacturers' Association
7 (DCMA) "Classification and Description of the Mixed Metal
8 Oxide Inorganic Colored Pigments", Second Edition, January,
9 1982. These pigments are "ceramic colorants:", for example,
10 compounds of oxides of different transition elements or
11 compounds of oxides of transition elements and of metal
12 oxides of elements of the main groups of the Periodic
13 System, e.g., having the spinel-type structure, and also
14 compounds such as zirconium silicate, zirconium oxide or tin
15 oxide, the crystal lattice of which contains ions of
16 transition metals or rare earth metals, as e.g., in
17 zirconium vanadium blue, in zirconium praseodyme yellow and
18 in zirconium iron pink, or the cadmium sulfides and cadmium
19 sulfo selenides as well as inclusion pigments containing such
20 compounds, e.g., based on zirconium silicate, tin oxide,
21 zirconium oxide or quartz.

22 Examples of typical ceramic colorants are cobalt
23 aluminates, chrome tin pink sphere, chrome tin orchid
24 cassitorite, tin vanadium yellow, zirconium praseodyme
25 yellow, zirconium iron pink, the cadmium sulfo selenides and
26 cadmium sulfides and the inclusion compounds containing
27 them, e.g., zirconium silicate, tin oxide, zirconium oxide
28 or quartz; copper-red, manganese pink, colcothar, the iron
29 oxide brown pigments such as iron oxides, iron-chrome-
30 alumina spinels, manganese-alumina spinels, wine-chrome
31 spinels, iron-alumina spinels, zinc-iron spinels, nickel-
32 iron spinels, manganese-chrome spinels, zinc-iron-chrome
33 spinels, tin oxide, titanium dioxide and titanates, e.g.,

1 nickel-antimony titanate, chrome-antimony titanate or
2 manganese-antimony titanate.

3 Preferred pigments are zirconium vanadium yellow,
4 praseodyme yellow, the iron oxide brown pigments such as
5 zinc-iron-chrome spinels and zirconium iron pink, titanium
6 dioxide, titanates, cadmium sulfides and cadmium
7 sulfoselenides as well as inclusion pigments containing such
8 compounds.

9

10 **Organic Pigments Useful in Marking Materials:**

11 Organic pigments are intensely colored, particulate
12 organic solids that are essentially insoluble in, and
13 physically and chemically unaffected by the vehicle or
14 substrate into which they are incorporated.

15 Characteristics of Organic Pigments

16 Bright, pure, rich colors

17 More expensive than inorganic pigments

18 Less resistant to sunlight, humidity, and
19 chemicals

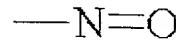
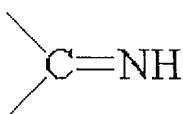
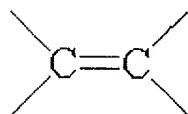
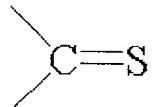
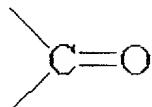
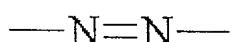
20 Key raw materials are petroleum based

21

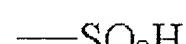
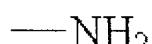
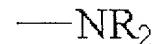
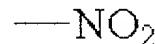
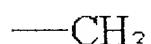
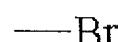
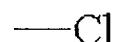
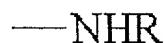
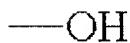
22 Color is produced in compounds by selective absorption
23 and reflectance of specific wavelengths of the visible
24 spectrum. Selective effect arise from the presence of
25 vibrating (resonating) electrons in the structure of a
26 molecule or molecular group. If a molecule absorbs in the
27 visible range, it possesses a color complementary to that
28 which is absorbed. Thus, a compound absorbing in the violet
29 is seen as yellow. Chemical groups which cause absorption
30 and give rise to color are called chromophores. Groups
31 which intensify or modify color are known as auxochromes.

32

1 Some examples of chromophore chemical groups include:
2



11 Some examples of auxochrome chemical groups include:
12

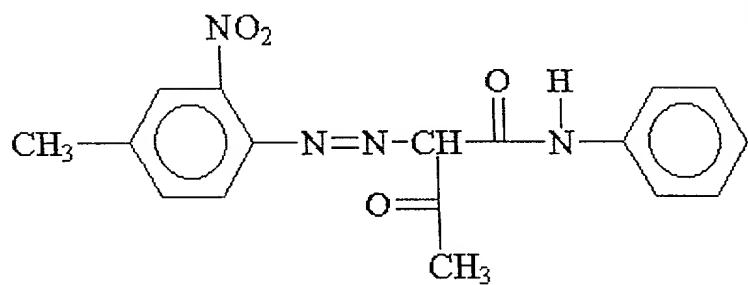
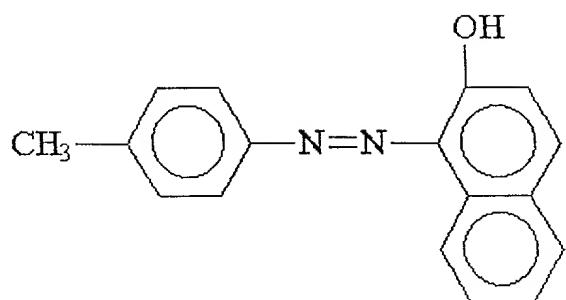


R. H. Hill, Jr., *Handbook of Organic Compounds*, Marcel Dekker, New York, 1970.

33 Organic pigments are divided into six categories:

1. Monoazo pigments
2. Diazo pigments
3. Acid and base dye pigments
4. Phthalocyanine pigments
5. Quinacridone pigments
6. Other polycyclic pigments

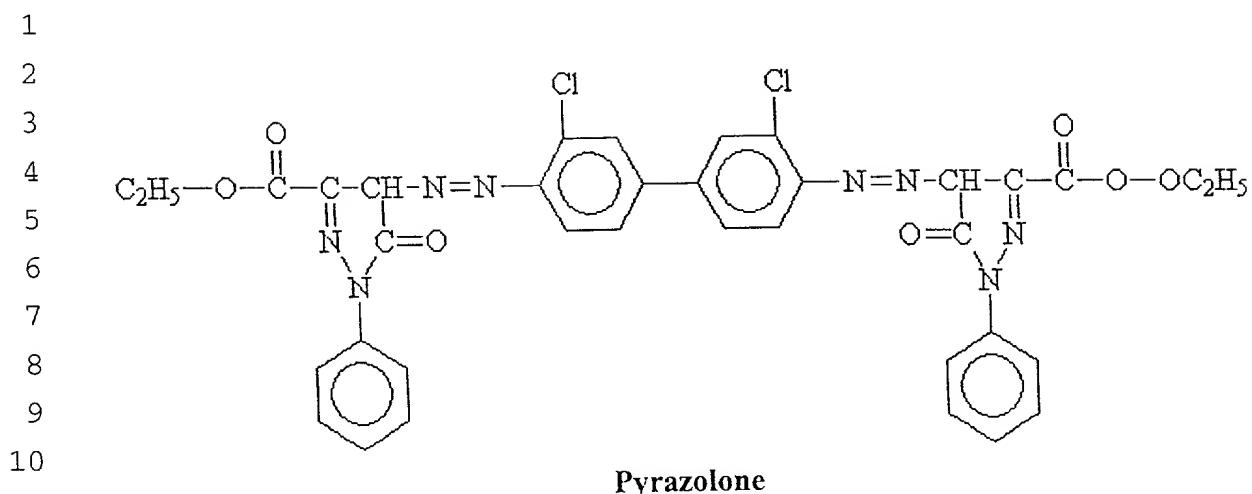
1 Some azo pigments include:



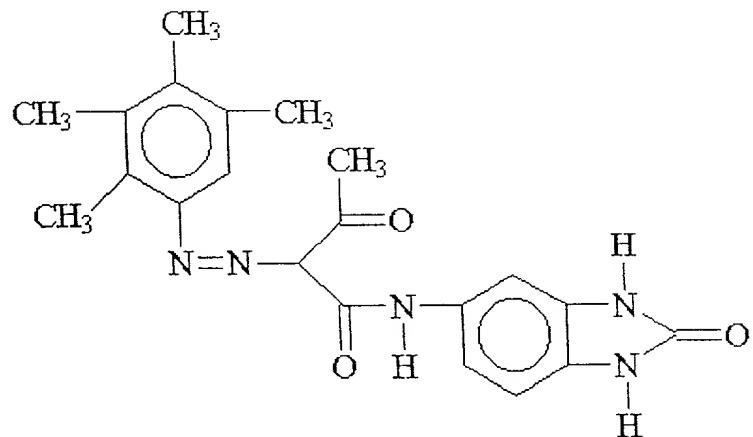
Pigment Red 3

Monoazo Yellow

Pigment Yellow 12 ($C_{32}H_{26}Cl_2N_6O_4$) is a yellow diazo pigment. C.I. No. 21090. See diazotization. Preparation: Condensation of 3,3'-dichlorobenzidine di-diazotate with acetoacetanilide. Uses: Printing inks; lacquers resistant to heat and solvents; in rubber and resins; in paper coloring, textile printing.



14 Benzimidazolone Pigments:
 15
 16
 17
 18
 19
 20
 21
 22
 23
 24
 25
 26
 27 Hansa Yellow
 28



1 Phthalocyanine Pigments are the single most successful class
2 of organic pigments, and include:

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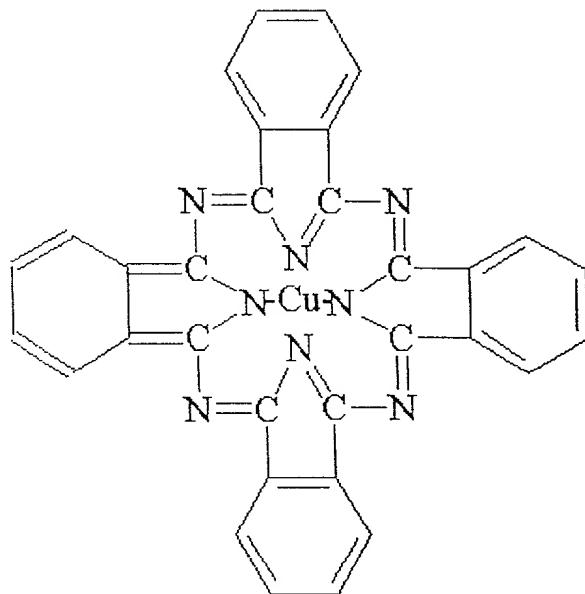
13

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18 Phthalocyanine Blue

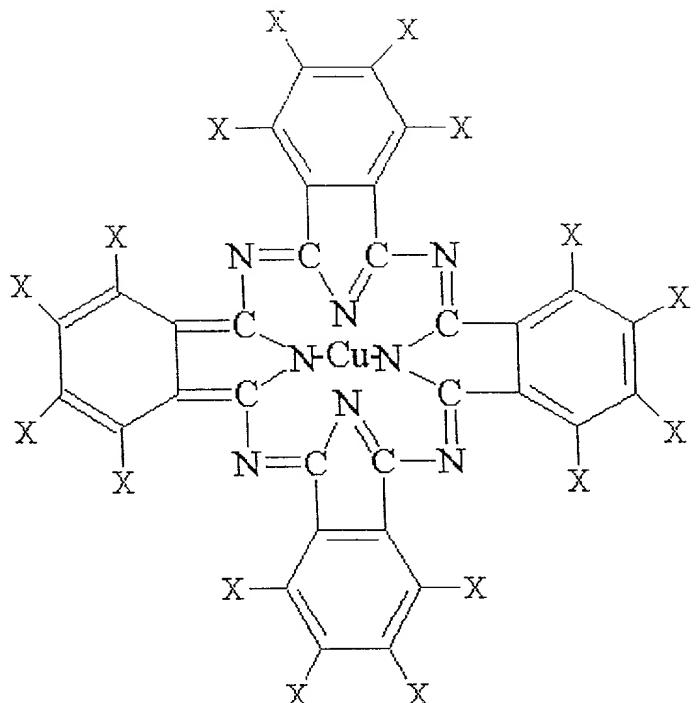
19

20

21

22 Pigment Blue 15 ($C_{32}H_{16}N_8Cu$) is a bright blue copper
23 phthalocyanine pigment (q.v.). C.I. No. 74160. Preparation:
24 By heating phthalonitrile with cuprous chloride. Uses: In
25 paints; alkyd resin enamels; printing inks; lacquers;
26 rubber; resins; papers; tinplate printing; colored chalks
27 and pencils.

28



Phthalocyanine Green

(X = H, Cl or Br, empirical formula $C_{32}H_xN_8Cl_yBr_zCu$ $x + y + z = 16$)

19 Pigment Green 7 ($C_{32}O_{o-1}N_8Cl_{15-16}Cu$) is a bright green
20 chlorinated copper phthalocyanine pigment (q.v.). C.I. No.
21 74260. Derivation: Heating copper phthalocyanine in sulfur
22 dichloride under pressure. Uses: Paints; printing inks;
23 lacquers; leather and book cloth; paper surfacing; chalks;
24 colored pencils.

26 Major reasons for use:

Excellent stability to solvents, heat, light, and weathering

29 High tinctorial strength

30 Cost effectiveness

31 Consistency and uniqueness of shades

32 Completely non-toxic

1 Pigment Blue 24 ($C_{37}H_{34}N_2O_9S_3Na_2$) is a bright greenish blue
2 triarylmethane pigment (q.v.). C.I. No. 42090. Uses: In
3 printing inks, especially for tinplate printing; in rubber;
4 plastics; artist colors; lacquers.

5

6 Pigment Blue 19 ($C_{32}H_{28}N_3O_4SNa$) is a bright blue to bright
7 reddish navy triphenylmethane pigment (q.v.). C.I. No.
8 42750A. Use: Coloring for candles.

9

10 Carbon black, although sometimes classified as
11 inorganic and not considered to have "positive color value",
12 is considered an organic pigment for the purposes of the
13 invention, also functioning as an energy absorbing enhancer.
14

15 **Radiant Energy Sources**

16 Examples of laser or diode based energy sources to be
17 used are solid state pulsed and/or CW lasers such as ruby
18 lasers or frequency multiplied Nd:YAG lasers, pulsed lasers
19 with booster such as pulsed dye lasers or Raman shifter, and
20 also continuous-wave lasers with pulse modifications (Q-
21 switch, mode locker), for example, on the basis of CW Nd:YAG
22 lasers with frequency multiplier or CW ion lasers (Ar, KR),
23 as well as pulsed metal vapor lasers; for example, copper
24 vapor lasers or gold vapor lasers, or high-capacity pulsed
25 or continuous wave semi-conductor diode lasers, and also
26 pulsed gas lasers such as CO₂ and excimer lasers.

27 What is generally preferred is a low-power (i.e., about
28 six watts or less), low-cost continuous-wave diode laser.
29 Any of the other higher power lasers need to have the power
30 partially attenuated by known means including mechanical
31 apertures and/or neutral-density filters and/or polarizers
32 and/or low-efficiency mirrors.

1 The wavelength to be selected for the laser or diode
2 based energy source is that at which the marking material,
3 with or without the energy absorbing enhancer absorbs the
4 radiation most efficiently.

5 Several different methods are suitable for laser
6 marking, for example: a) the mask method whereby the area to
7 be marked is uniformly coated with the marking material and
8 the radiant energy passes through a fixed, data specific
9 mask and impinges onto the marking material to produce the
10 desired mark; and b) the dot-matrix method whereby the area
11 to be marked is uniformly coated with the marking material
12 and the radiant energy passes through a computer controlled,
13 changeable data, dot-matrix mask and impinges onto the
14 marking material to produce the desired mark; and c) the
15 beam deflection method whereby the area to be marked is
16 uniformly coated with the marking material and the radiant
17 energy passes through a beam steering head and impinges onto
18 the marking material to produce the desired mark; and d) the
19 X - Y plotter method whereby the area to be marked is
20 uniformly coated with the marking material and the radiant
21 energy moves on a gantry type X - Y mechanism utilizing
22 mirrors and/or fiber-optics and impinges onto the marking
23 material to produce the desired mark; and e) the part moving
24 method whereby the area to be marked is uniformly coated
25 with the marking material and the workpiece to be marked is
26 moved using an X - Y motor driven stage under a stationary
27 beam which impinges onto the marking material to produce the
28 desired mark; and f) the area irradiation method whereby
29 data specific marking material is uniformly applied to the
30 surface of the workpiece and the data specific marking area
31 is irradiated by means of a beam steering mechanism or by
32 means of moving the workpiece under a stationary beam. In
33 methods b), c), d), e) and f) the laser is preferably

1 combined with a laser marking system so that the marking
2 material can be irradiated with any, e.g., computer
3 programmed, digits, letters and special symbols where the
4 laser beam strikes the marking material in the most
5 efficient manner possible.

6 In one important aspect of the invention, the marking
7 materials can be formulated to absorb a narrow band of
8 wavelengths, e.g., approximately 1 micron, and will react
9 with the substrate material when the proper temperature is
10 achieved. In this way, a single radiant energy source
11 (laser or diode) can be employed to mark all materials.

12 Suitable substrate materials which can be marked
13 include conductive materials, such as:

14 metals, ferrous and non-ferrous, which can be pure
15 elemental metals, alloys, and include coatings or plating
16 layers having similar properties; and

17 conductive polymer compositions, which can be
18 intrinsically conductive due to physico-chemical properties
19 or filled with conductive fillers, fibers and the like.

20 A variety of nonconductive or dielectric materials are
21 also suitable for marking, but will normally require coating
22 with a conductive material before the marking material(s)
23 are applied by electrostatic methods. For example, all
24 types of glasses, whether conventional or specialized as
25 with optical glasses, glasses incorporating nuclear waste
26 for storage and others, may be employed. Similarly,
27 ceramics of all types, including those based upon alkali
28 metal and alkaline earth metal carbonates and the like or
29 ceramic compounds combining at least two of the elements
30 carbon, silicon and nitrogen without oxygen can be used.
31 Various baked porcelain compositions can also be employed.
32 Semiconductors, which are neither clearly conductive nor
33 completely dielectric, can also be employed, but may require

1 conductive coatings before electrostatic application of
2 marking materials.

3 A wide variety of commercial polymeric materials or
4 plastics can be employed as substrates in the present
5 invention. A plastic is made up principally of a binder
6 together with plasticizers, fillers, pigments, and other
7 additives. The binder gives a plastic its main
8 characteristics and usually its name. Thus, polyvinyl
9 chloride is both the name of a binder and the name of a
10 plastic into which it is made. Binders may be natural
11 materials, e.g., cellulose derivatives, casein, or milk
12 protein, but are more commonly synthetic resins. In either
13 case, the binder materials consist of very long chainlike
14 molecules called polymers. Cellulose derivatives are made
15 from cellulose, a naturally occurring polymer; casein is
16 also a naturally occurring polymer. Synthetic resins are
17 polymerized, or built up, from small simple molecules called
18 monomers. Plasticizers are added to a binder to increase
19 flexibility and toughness. Fillers are added to improve
20 particular properties, e.g., hardness or resistance to
21 shock. Pigments are used to impart various colors. Virtually
22 any desired color or shape and many combinations of the
23 properties of hardness, durability, elasticity, and
24 resistance to heat, cold, and acid can be obtained in a
25 plastic.

26 There are two basic types of plastics: thermosetting,
27 which cannot be resoftened after being subjected to heat and
28 pressure; and thermoplastic, which can be repeatedly
29 softened and remolded by heat and pressure. When heat and
30 pressure are applied to a thermoplastic binder, the
31 chainlike polymers slide past each other, giving the
32 material plasticity. However, when heat and pressure are
33 initially applied to a thermosetting binder, the molecular

1 chains become cross-linked, thus preventing any slippage if
2 heat and pressure are reapplied.

3 Some typical plastics are: epoxy resins; polyacrylics;
4 polycarbonates; polyethylenes; polyolefins; polypropylenes;
5 polystyrenes; polyurethanes; polyvinyl chlorides; vinyl
6 plastics. Most of these materials will be dielectrics,
7 unless they are synthesized or filled to create conductive
8 materials. Such polymers can be thermoplastic or
9 thermosetting, and can be solid or slightly pliable under
10 ambient conditions. Exemplary families of polymers include
11 the polyethylenes, polypropylenes, polybutenes and various
12 forms of synthetic and natural rubbers, polyvinyl chlorides,
13 mylars, nylons, polyarylene sulfides, polystyrenes,
14 polytetrafluoroethylenes (PTFE), polyacrylates of various
15 types, and copolymers of many of the preceding. Due to the
16 generally low level of power used to create the markings,
17 the methods of the invention can be used to mark cast
18 objects of trinitrotoluene (TNT) and similar military and
19 commercial explosives, provided that the objects are first
20 provided with conductive coatings and the marking materials
21 electrostatically applied. An advantage of the present
22 invention is that it provides permanent marking upon
23 "slippery" plastics such as nylon and PTFE.

24 Although the present invention has been described with
25 reference to preferred embodiments, numerous modifications
26 and variations can be made and still the result will come
27 within the scope of the invention. No limitations with
28 respect to the specific embodiments disclosed herein are
29 intended or should be inferred.

30
31